



(19)

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 624 680 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
16.10.2002 Bulletin 2002/42

(51) Int Cl.7: D06M 13/298

(21) Application number: 93902529.2

(86) International application number:
PCT/JP93/00089

(22) Date of filing: 26.01.1993

(87) International publication number:
WO 93/015254 (05.08.1993 Gazette 1993/19)

(54) USE OF A TREATMENT AGENT FOR FIBER PRODUCT, METHOD OF TREATING FIBER PRODUCT, AND FIBER PRODUCT TREATED THEREBY

VERWENDUNG EINES BEHANDLUNGSMITTELS FÜR FASERPRODUKTE, VERFAHREN ZUM BEHANDELN VON FASERPRODUKTEN UND DIE DADURCH BEHANDELTN FASERPRODUKTE

UTILISATION D'UN AGENT DE TRAITEMENT POUR PRODUITS FIEREUX, PROCEDE DE TRAITEMENT DE PRODUITS FIBREUX ET PRODUITS FIBREUX TRAITES SELON CE PROCEDE

(84) Designated Contracting States:
DE ES FR GB IT

• SANO, Taro, Yodogawa Works of Daikin Ind. Ltd.
Settsu-shi, Osaka 566 566 (JP)
• KUBO, Motonobu,
Yodogawa Works of Daikin Ind. Ltd.
Settsu-shi, Osaka 566 (JP)

(30) Priority: 27.01.1992 JP 1188392

(74) Representative:
Hansen, Bernd, Dr. Dipl.-Chem. et al
Hoffmann Eitle,
Patent- und Rechtsanwälte,
Arabellastrasse 4
81925 München (DE)

(43) Date of publication of application:
17.11.1994 Bulletin 1994/46

(56) References cited:

(73) Proprietor: DAIKIN INDUSTRIES, LTD.
Kita-ku, Osaka 530 (JP)

EP-A- 0 340 753	FR-A- 2 270 364
FR-A- 2 374 327	JP-A- 2 215 900
JP-A- 53 060 970	JP-A- 60 064 990
JP-B- 35 004 747	US-A- 3 083 224
US-A- 3 096 207	

(72) Inventors:

- HARA, Kazuto,
Yodogawa Works of Daikin Ind. Ltd.
Settsu-shi, Osaka 566 (JP)
- ITAMI, Yasuo,
Yodogawa Works of Daikin Ind. Ltd.
Settsu-shi, Osaka 566 (JP)
- MASUTANI, Tetsuya,
Yodogawa Works Daikin Ind. Ltd
Settsu-shi, Osaka 566 (JP)
- NOSE, Nobuyuki,
Yodogawa Works of Daikin Ind. Ltd
Settsu-shi, Osaka 566 (JP)
- ENOMOTO, Takashi,
Yodogawa Works of Daikin Ind Ltd
Settsu-shi, Osaka 566ka 566 (JP)
- UEDA, Akihiko,
Yodogawa Works of Daikin Ind. Ltd.
Settsu-shi, Osaka 566 566 (JP)

- Microfilm of the specification and drawings
annexed to the written application of Japanese
Utility Model Application No. 78030/1985
(Laid-Open No. 198298/1986) (Kuraray Co., Ltd.),
December 11, 1986 (11.12.86).
- Japan Textile Machinery Society, "The latest
fiber working technology", September 25, 1973
(25.09.73), p. 120-129.

EP 0 624 680 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description**BACKGROUND OF THE INVENTION**5 **Field of the Invention**

[0001] The present invention relates to the use of an agent for treating a textile, a method for treating a textile and a treated textile.

10 **Related Art**

[0002] Hitherto, Japanese Patent Kokoku Publication Nos. 4503/1968 and 4770/1973 as well as Japanese Patent Kokai Publications JP-A-60-64990 and JP-53-50079 disclose that a fluorine-containing phosphate ester and a fluorine-containing phosphonic acid can give oil-repellency to a textile and a paper. However, when the fluorine-containing color shade and the softness of treated material are deteriorated because of the treatment, the initial water- and oil-repellency is insufficient and above properties are remarkably deteriorated by a wash and/or rub.

[0003] Japanese Patent Kokai Publication No. 215900/1990 discloses a method for treating a leather with a fluorine-containing phosphoric acid compound and a cationic compound. However, this document does not disclose the treatment of the textile which is required to have the good touch, feeling, color shade and softness. USP 2,662,835 discloses a method for treating a fiber material with a chromium complex salt of a fluorine-containing carboxylic acid. However, this document does not disclose the water- and oil-repellency and the method of this document gives no sufficient effect even if used in a high concentration, and gives remarkably discolored fibers.

[0004] USP 3,096,207 discloses a method for treating a leather and a fiber with a fluorine-containing phosphoric acid compound or a metal salt thereof. However, since this document discloses the treating agent and treating method which are different from those of the present invention, this document gives the worse effect and durability than the present invention.

Furthermore, in the JP Utility Model Laid open No. 198298/1986 a flame-retardant stain proofing carpet is described which comprises, *inter alia*, a phosphorous or halogen-containing flame-retardant compound.

[0005] By the way, a fluorine-containing polymeric compound which is generally used, for example, an acrylic polymeric compound containing a fluoroalkyl group is used for the treatment, the treated textile suffers from the disadvantages that the originally possessed touch, feeling, softness and the like are remarkably deteriorated because of the treatment and that the above properties and water- and oil-repellency are remarkably deteriorated when the textile is washed or rubbed. The initial performances are very poor for a nylon having high hydrophilic property and the other fibers. It is known that, in the case that the textile is slightly washed, the performances are recovered to some extent by the use of a heating treatment such as a process for ironing the textile. But, an operation of the heating treatment is very troublesome.

[0006] Recently, in order to improve the durability, when an acrylic polymer containing a fluoroalkyl group is used for the treatment, an auxiliary is used together. Specific examples of the auxiliary are a melamine resin and a urea resin. When these resins are used together with the acrylic polymer, the deterioration of the feeling of the fibers tends to be more significant than that of the fibers treated with that the polymer alone. It seems that the durability has the relationship contrary to the softness when the fluorine-containing polymer is used.

[0007] The acrylic polymer having the fluoroalkyl group has a low glass transition temperature (T_g). When the temperature of the acrylic polymer is higher than T_g , the arrangement of the fluoroalkyl group causing the water- and oil-repellency is disordered so that the water- and oil repellency is remarkably decreased. Therefore, the acrylic polymer is very weak to hot water, and lacks in the hot water repellency.

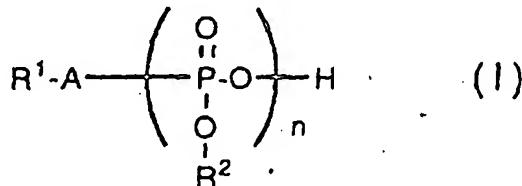
[0008] As stated above, when any of the conventional treating agents and methods is used, the properties originally possessed by a natural or synthetic fiber are deteriorated by the treatment and the water- and oil-repellency given by the treatment is deteriorated by a wash and the like.

50 **SUMMARY OF THE INVENTION****Problems to be solved by the invention**

[0009] An object of the present invention is to keep the touch, feeling, color shade (clarity), and softness originally possessed by the fibers even after the treatment, to keep the above properties even after a long time use including a wash and to impart hot water-repellency, durable water- and oil repellency and soil releasability.

Means for solving the problems

[0010] According to one aspect, the present invention uses an agent for treating a textile, comprising a combination of a modifying agent and a fixing agent, wherein the modifying agent is a fluorine - containing phosphor derivative 5 represented by the formula:



15 wherein R¹ and R² are, same or different, a hydrogen atom or R_f(CH₂)_m-(wherein R_f is a saturated or unsaturated, linear or branched fluorine-containing aliphatic group having 4 to 20 carbon atoms in which an oxygen atom, a nitrogen atom, a sulfonyl group and/or an aromatic ring may be inserted between the carbon atoms; and m is 1 or 2) (R¹ and R² are not simultaneously a hydrogen atom),

20 A is an oxygen atom, a sulfur atom or a direct bond; and n is 1 or 2, and having a molecular weight of not larger than 2,000 or a salt thereof, and the fixing agent is a metal salt compound.

[0011] According to a second aspect, the present invention provides a method for treating a textile with said treating agent.

25 [0012] According to a third aspect, the present invention provides a textile treated with said treating agent.

[0013] According to a fourth aspect, the present invention provides a method for treating a textile, comprising two steps of

treating the textile with said treating agent; and then

30 treating the textile with a fluorine-containing water- and oil - repellent or a fluorine-containing stainproofing agent.

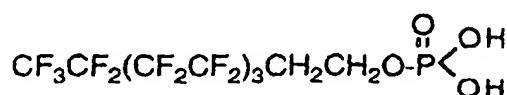
DETAILED DESCRIPTION OF THE INVENTION

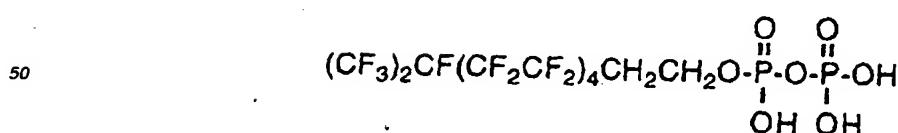
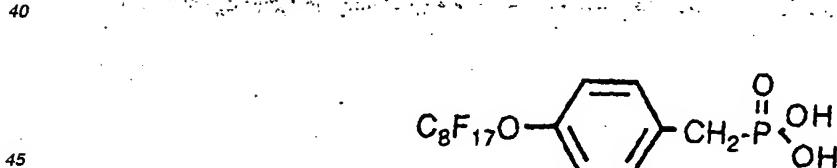
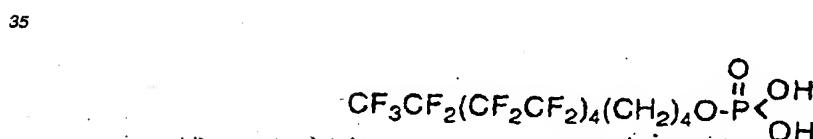
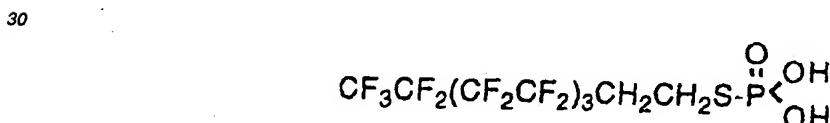
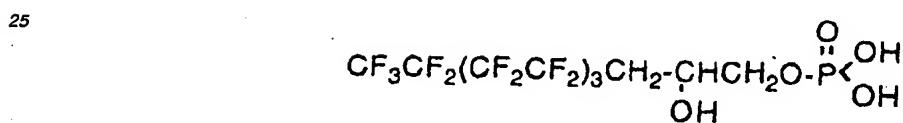
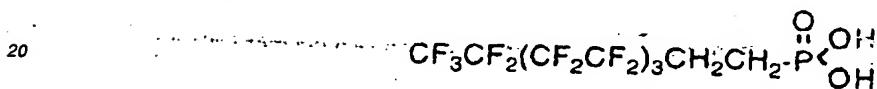
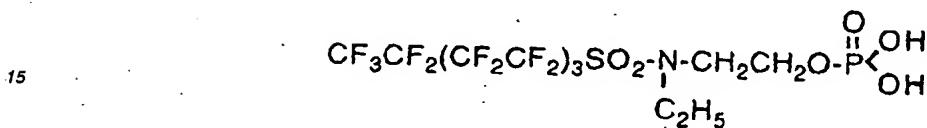
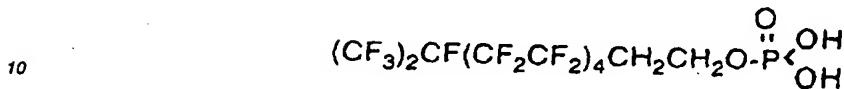
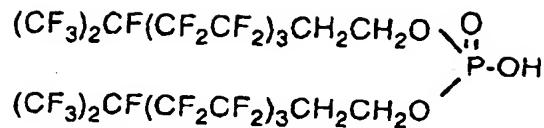
[0014] In the present invention, after the textile is treated with the fixing agent, the textile may be treated with the modifying agent. Alternatively, after the textile is treated with the modifying agent, the textile may be treated with the fixing agent.

35 [0015] In the present invention, the use of the combination of the modifying agent and the fixing agent can keep the touch, feeling, color shade and softness originally possessed by the fibers for a long time, and can give a strong bond, between the fibers and the fluorine - containing phosphor derivative so that the exfoliation of the fluorine-containing phosphor derivative from the fibers is prevented.

40 [0016] According to the present invention, the modifying agent is the fluorine-containing phosphor derivative of the above formula (1) or the salt thereof. The fluorine-containing phosphor derivative is a compound which has both of a P-OH linkage and an organic fluorine - containing group. The organic fluorine-containing is usually a fluorine - containing aliphatic group, particularly a saturated or unsaturated, linear or branched fluorine-containing aliphatic group and includes a group in which an oxygen atom, a nitrogen atom, a sulfonyl group and/or an aromatic group intervene in a 45 carbon-carbon linkage. Specific examples of the salt of the fluorine-containing phosphor derivative are a salt of a monovalent metal such as a sodium salt, a potassium salt, a lithium salt and the like, an organic amine salt such as a diethanolamine salt, a triethylamine salt, a propylamine salt, a morpholine amine salt and the like, and an ammonium salt. These compounds have water- and oil-repellency.

50 [0017] Specific examples of the fluorine-containing phosphor derivative are as follows and are not limited to the following compounds:





50

55

[0018] In the present invention, a metal in the metal salt compound used as the fixing agent can ionically bond to a hydroxyl group bonding to a phosphorus atom, may be a metal having the valency of at least two and may be preferably chromium, zirconium, titanium, aluminum or the like. In view of the color shade, zirconium, titanium, aluminum and the like are more preferable. The metal salt compound is preferably water-soluble and is preferably, for example, a chloride, a nitrate salt, a sulfate salt, a hydroxide and the like.

[0019] In the present invention, the treated textile may be in the form of a fiber as such, or a yarn, a woven fabric, a knitted fabric, a nonwoven fabric and the like which are formed from the fibers.

Specific examples of the textile are a natural fiber such as cotton, wool and silk; and a chemical fiber including a synthetic fiber such as an acryl, a nylon, a cellulose, a polyester and the like. The present invention is particularly effective to a protein fiber and a polyamide fiber such as silk and nylon. The present invention is suitable for a yarn, or a woven, knitted or nonwoven fabric formed from recently significantly developed extra fine fibers, particularly an artificial leather which is one of nonwoven fabrics formed from the extra fine fibers in view that the feeling and touch are important. The extra fine fiber has not larger than 0,11 tex (1 denier), preferably from 0,11 - 0,000011 tex (1 to 0.0001 denier), more preferably from 0,011 to 0,00011 tex (0.1 to 0.001 denier). The textile suitable for the present invention is a carpet. After forming the carpet from the yarn, the carpet may be treated according to the present invention. Alternatively, after treating the yarn according to the present invention, the carpet may be formed from the yarn.

[0020] In the present invention, the used carpet may be made of any of materials such as a polyamide such as a nylon, a polyester and an acryl and the material of the carpet is not limited. The present invention is particularly suitable for a nylon carpet which is usually used under severe conditions. The structure, the weave design, the pile length of the carpet are not limited.

[0021] According to the present invention, the textile is treated with the above agent for treating the textile. Anyone of the modifying agent and the fixing agent may be used earlier as described below. The treating method with the modifying agent and the fixing agent includes the following methods (i), (ii) and (iii).

(i) Firstly, the method comprising treating the textile with the fixing agent and then with the modifying agent is explained. The textile is immersed in a solution of the fixing agent and pulled up from the solution, and water is squeezed from the textile. The textile is then immersed in a solution of the modifying agent; a solution of an acid is added to the solution of modifying agent to adjust pH of the solution of modifying agent to a range between 1 and 5, preferably between 3 and 4; the textile is kept standing; water is squeezed from the textile; the textile is sufficiently washed with water; water is squeezed from the textile; and the textile is dried. Alternatively, the textile is immersed in a solution of the modifying agent; water is squeezed from the textile; the textile is immersed in a solution of an acid; water is squeezed from the textile; the textile is sufficiently washed with water; water is squeezed from the textile; and the textile is dried.

(ii) The immersion in the fixing agent solution may be conducted after the immersion in the modifying agent solution. Firstly, the textile is immersed in a solution of the modifying agent; the textile is pulled up from the solution and water is squeezed from the textile. Then, the textile is immersed in a solution of the fixing agent; a solution of an acid is added to the solution of the fixing agent to adjust pH of the solution of the fixing agent to a range between 1 and 5, preferably between 3 and 4; the textile is kept standing; water is squeezed from the textile; the textile is sufficiently washed with water; water is squeezed from the textile; and the textile is dried. Alternatively, the textile is immersed in the solution of the fixing agent; water is squeezed from the textile; the textile is immersed in a solution of an acid; the water is squeezed from the textile; the textile is sufficiently washed with water; water is squeezed from the textile; and the textile is dried.

(iii) Alternatively, a series of the above procedures can be conducted in the same bath. For example, after the textile is immersed in a solution of the fixing agent, and the modifying agent is added to the solution to immerse the textile in the solution. Further, a solution of an acid is added to the solution containing the fixing agent and the modifying agent to adjust pH of the solution to a range between 1 and 5, preferably between 3 and 4, the textile is kept standing in the solution, water is squeezed from the textile, and the textile is sufficiently washed with water. Then water is squeezed from the textile and the textile is dried. After the textile is immersed in the solution of the modifying agent, the fixing agent or the solution thereof may be added.

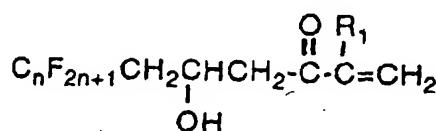
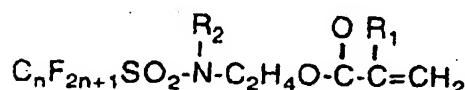
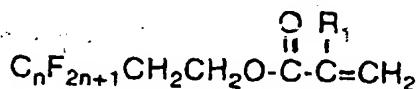
[0022] In the above methods (i), (ii) and (iii), the solution of the fixing agent is usually an aqueous solution containing usually 0.001 to 20 % by weight, preferably 0.01 to 10 % by weight of the fixing agent, based on the weight of the treated textile. The temperature of the solution of the fixing agent is usually from 20 to 70°C. The solution of modifying agent is usually an aqueous or alcoholic solution containing usually from 0.001 to 50 % by weight, preferably from 0.01 to 20 % by weight of the modifying agent, based on the weight of the treated textile. The temperature of the solution of the modifying agent is usually from 5 to 90°C, preferably from 20 to 70°C. The solution of the acid which is used for the immersion or the adjusting of pH is a solution, preferably an aqueous solution containing a mineral acid such as hydrochloric acid and sulfuric acid, or an organic acid such as formic acid, acetic acid and propionic acid. The concentration of the solution of the acid is not limited and is usually from 0.05 to 30 % by weight, preferably from 0.1 to 5 % by weight. The temperature of the solution of the acid is usually from 5 to 90°C, preferably from 20 to 70°C. The time during which the textile is immersed in the fixing agent solution, the modifying agent solution or the acid solution is usually at least 10 seconds, preferably from 1 to 120 minutes, more preferably from 1 to 30 minutes. The standing time in the bath having the adjusted pH of 1 to 5 is usually at least 10 seconds, preferably from 1 to 30 minutes. The drying

temperature is usually from 10 to 70°C, preferably a room temperature. The drying time varies according to the drying conditions (particularly the drying temperature), but is usually not larger than 24 hours, preferably from 0.1 to 10 hours. When the immersion is conducted in the same bath, a weight ratio of the fixing agent to the modifying agent is usually from 0.1:1 to 10:1.

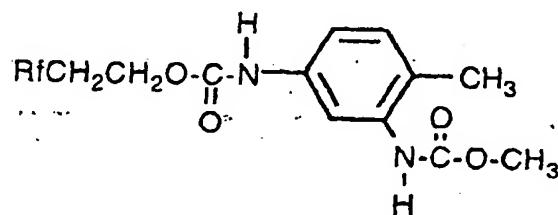
[0023] In the present invention, if necessary, another treating agent or treating method may be used together with the agent and method of the present invention. For example, the treatment with a conventional fluorine-containing water- and oil-repellent, the softening finish with a silicone, and the resin treatment can be used. A fluorine-containing stainproofing agent may be used. It is preferable to use the treatment with the fluorine-containing water- and oil-repellent or the fluorine - containing stainproofing agent depending on the use.

[0024] In the present invention, other treating agent or additive, for example, a soil release (SR) agent, an antistatic agent, a flame retardant, an anti-fungus agent and a non-shrinking agent may be used.

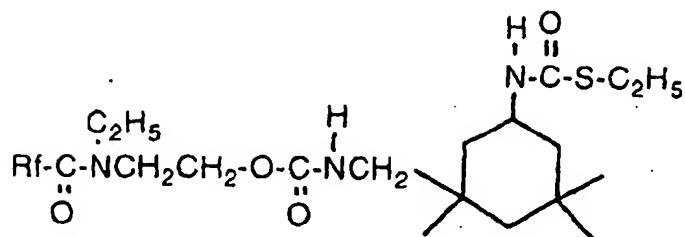
[0025] In the present invention, a typical example of the fluorine - containing water- and oil-repellent which is used in the second step of the treatment is a conventional well-known fluorine-containing water-and oil-repellent having a perfluoroalkyl group as a side chain. Specific examples of the fluorine-containing water- and oil-repellent are polymers and copolymers of the following monomers:



40 wherein R₁ is a hydrogen atom or a methyl group, R₂ is a methyl group or an ethyl group, and n is an integer of 5 to 21.
[0026] In the present invention, the fluorine-containing stainproofing agent used in the second step may be a poly-
fluoroalkyl group-containing urethane compound, a polyfluoroalkyl group-containing ester compound or the like. Typical
examples of the fluorine-containing stainproofing agent may be the following compounds, but are not limited to the
following compounds. For example, the above compounds mentioned as the fluorine-containing water- and oil repellent
can be used as the fluorine-containing stainproofing agent. A silicone stainproofing agent can be used instead of the
fluorine-containing stainproofing agent.

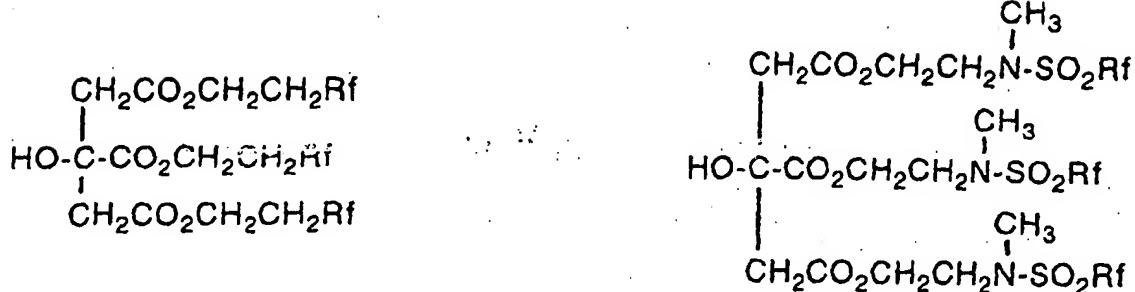


5

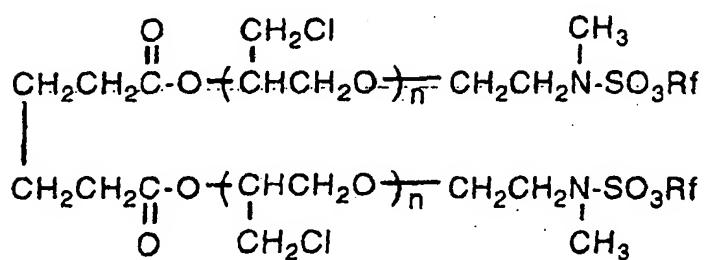


10

15



25



35

wherein R_f is C_nF_{2n+1} (n is an integer of 5 to 21).

[0027] The fluorine-containing stainproofing agent may be used together with various auxiliaries such as a melamine resin, a urea resin, a blocked isocyanate, and glyoxal.

40 [0028] In the second step, the textile which has been treated in the first step is treated with the fluorine-containing water- and oil - repellent or the fluorine-containing stainproofing agent. The second step may be conventionally used treatment, for example, a spraying technique, a foam technique, an immersion technique, an impregnation technique, a padding technique or a coating technique is used, and then the textile is dried. An auxiliary such as a melamine resin or a urea resin may be used together with the fluorine-containing water- and oil - repellent or the fluorine-containing stainproofing agent. If necessary, further, a thermal treatment or a calendering may be further conducted. A treating agent other than a fluorine-containing compound (such as a silicone compound) may be used together.

45 [0029] The used fluorine-containing water- and oil repellent and fluorine-containing stainproofing agent may be in the form of any of an emulsion and an solution in an organic solvent. In the case of the aqueous emulsion, it is preferable to add, to the emulsion, a watersoluble lower alcohol or ketone (isopropyl alcohol is particularly preferable) in an amount of 0.1 to 10 % by weight, more preferably from 1 to 5 % by weight based on the emulsion, since the fluorine-containing water- and oil-repellent and the like can easily penetrate in the textile.

50 [0030] The two steps can be conducted for any of textiles. For example, the first and second steps may be conducted for the finished carpet. Alternatively, the first and second steps may be conducted for a raw yarn or fiber used for the carpet, and then the carpet can be formed from the treated yarn or fiber. Alternatively, the first step may be conducted for the raw yarn or fiber and then the second step may be conducted for the finished carpet.

55 [0031] Since a complex is formed between the fluorine-containing phosphor derivative and a metal coordinated or fixed to a bundle of fibers, the present invention can keep the touch, the feeling, the color shade (clarity) and the softness originally possessed by the fibers and can give the keeping of the above properties for a long time and durable

water- and oil-repellency which are not given by the conventional agents for treating the textile. Since in the present invention, the fluorine-containing phosphor derivative is penetrated in the bundle of fibers and then fixed, the present invention does not suffer from the disadvantage that only the surface of fabric has the water- and oil-repellency. In the present invention, even if the textile is thick, internal parts of the textile can have the good properties. The present invention can give the same effect to various forms of the textiles, such as the fiber, the yarn, the woven fabric, the knitted fabric, the nonwoven fabric and the like.

[0032] When the textile is treated with the agent for treating textile in the first step and then with the fluorine-containing oil- and water-repellent in the second step, the deterioration of the feeling and softness observed in the use of only the fluorine-containing water- and oil-repellent treatment is surprisingly improved. Even if the auxiliary such as the melamine resin, the blocked isocyanate and the like is used together, the present invention can give the unexpected effect that the treated textile has the same feeling as the feeling of the untreated textile. In addition, the durability of the water- and oil-repellency can be strengthened.

[0033] Since the textile of the present invention has the above advantages, it can be used for the application in which the textile is particularly required to have the good water- and oil-repellency and soil release property, for example, for the application in which the textile is subjected to wind and rain in outdoor. Specific examples of the application in which the textile is subjected to wind and rain are a tent, an automobile cover, a cover for two-wheeled vehicle, a convertible top for a load-carrying platform of a truck, a covering sheet for construction work, an umbrella, clothes [particularly, a rainwear (for example, a raincoat, a rain jacket and the like)], and the like. In addition, the textile is used for a hat, a cap, a foot wear (for example, shoes and slippers), a suitcase, a bag, a textile used for a cover of an article for sitting down (for example, a seat such as a car seat and a theater seat, a sofa and a chair), a curtain, a rug or mat, an interior article for a wall or ceiling of a built structure or vehicle (for example, an automobile, a train, an aircraft, a ship and the like), and various displays. Among the above applications, the present invention is preferable to the textile which is difficultly cleaned, the textile which is easily stained, and the textile which cannot be washed many times.

PREFERRED EMBODIMENT OF THE INVENTION

[0034] The present invention will be illustrated by the following Examples which do not limit the present invention. In the following Examples, % is by weight unless specified.

[0035] The water repellency shown in Examples 1-18 and Comparative Examples 1-10 is measured according to JIS (Japanese Industrial Standard) L-1092-1977 and expressed by the water repellency shown in the following Table 1. The water repellency shown in Examples 19-23 and Comparative Examples 11-14 is determined by quietly dropping several drops of a test isopropyl alcohol/water mixture shown in Table 2 on a surface of a sample, observing the penetration state of the drops after 3 minutes and expressing, as the water repellency, the maximum content of isopropyl alcohol in the drop keeping the shape of the drops. The oil repellency is measured according to AATCC TM-118-1975 and determined by dropping oils having different surface tensions shown in Table 3 on the sample and expressing, as a value of the oil repellency, the maximum value of the oil having no penetration after 30 seconds.

Table 1

Water repellency	State
100	No wet on the surface
90	Slight wet on the surface
80	Partial wet on the surface
70	Wet on the surface
50	Wet over the whole surface
0	Complete wet on the front and back surfaces

Table 2

Composition of mixture (vol %)	
Isopropyl alcohol	Water
0	100
10	90
20	80
30	70

Table 2 (continued)

Composition of mixture (vol %)	
Isopropyl alcohol	Water
40	60
50	50

Table 3

Oil repellency	Surface tension	Standard liquid
0	-	Inferior to 1
1	31.45	Nujol
2	29.6	Nujol/n-hexadecane = 65/35 (% by volume)
3	27.3	n-Hexadecane
4	26.35	n-Tetradecane
5	24.7	n-Dodecane
6	23.5	n-Decane
7	21.4	n-Octane
8	19.75	n-Heptane

[0036] The wash resistance is measured according to JIS-L-0217-103 and expressed by the water repellency and the oil repellency before and after washing the textile 20 times.

[0037] The hot water repellency is measured by the use of 75°C hot water according to JIS-L-1092-1977 and expressed in the same manner as in the water repellency.

[0038] The superscript "+" to the water repellency and the hot water repellency represents that the result is slightly better than said water repellency and said hot water repellency, respectively. The superscript "-" to the water repellency and the hot water repellency represents that the result is slightly inferior to said water repellency and said hot water repellency, respectively.

[0039] The dry soil releasability is measured according to JIS-L-1021-1979 as follows. A sample is stirred at 50 revolutions and contaminated with a dry soil having a composition shown in Table 4. After a residual soil of the sample is removed by the use of an electrical vacuum cleaner, the brightness of the sample surface is measured by a colorimeter and a contamination ratio is calculated according the following equation to evaluate the soil releasability of dry soil.

[0040] Contamination ratio (%) = $[(L_0 - L)/L_0] \times 100$ wherein L_0 is the brightness of the sample before the contamination, and L is the brightness of the sample after the contamination.

Table 4...

Components	% by weight
Peat moss	38
Cement	17
White clay	17
Diatomaceous earth	17
Carbon black	1.75
Ferric oxide	0.5
Nujol	8.75

[0041] The rub resistance is measured by the use of Gakushin-type friction tester according to JIS-L-0823-1971. A sample is rubbed 3,000 times under a load of 500 g, and the water- and oil-repellency of a rubbed part of the sample is evaluated to give the value of the rub resistance.

[0042] The feeling is evaluated by touching the sample according to the standard shown in Fig. 5.

Table 5

Rank	Feeling
O	Good

Table 5 (continued)

Rank	Feeling
Δ	Slightly poor
X	Poor

5

Example 1

[0043] Each of various textile fabric samples (nylon-6 taffeta, habutae silk and acrylic muslin; size: 20 cm x 20 cm square) was immersed in a 0.1 % aqueous solution of chromium sulfate (trade name: Bay Chrom F manufactured by Bayer AG) (a bath ratio of 50:1) at 40°C for 10 minutes, and water was squeezed from the sample. The sample was immersed in a 0.125 % aqueous solution of a Compound 11 (a fluorine-containing phosphor derivative) (a bath ratio of 40:1) shown in Table 6 at 40°C for 10 minutes. A 0.1 % aqueous solution of formic acid was added to the bath to adjust pH of the content in the bath to 3. The textile was kept standing in the bath for 10 minutes, water was squeezed from the textile, the textile was washed with water at 40°C and then the textile was dried at a room temperature. The touch, feeling, softness of each textile sample were evaluated before and after the treatment to reveal that these properties were the same before and after the treatment. These properties were the same before and after the washing. In addition, the water repellency and the oil repellency of each textile sample were measured before and after the washing. The results are shown in Table 7.

20

Example 2

[0044] The same procedure as in Example 1 was repeated except that a 0.1 % aqueous solution of zirconium sulfate (trade name: Brancorol ZB 33, manufactured by Bayer AG) was used instead of the aqueous chromium sulfate solution. The results are shown in Table 7.

25

Example 3

[0045] The same procedure as in Example 1 was repeated except that a 0.1 % aqueous solution of aluminum chloride (trade name: Lutan FS, manufactured by BASF AG) was used instead of the aqueous chromium sulfate solution. The results are shown in Table 7.

30

Example 4

[0046] The same procedure as in Example 1 was repeated except that a Compound 12 shown in Table 6 was used as the fluorine-containing phosphor derivative. The results are shown in Table 7.

35

Example 5

[0047] The same procedure as in Example 2 was repeated except that a Compound 12 shown in Table 6 was used as the fluorine-containing phosphoric acid derivative. The results are shown in Table 7.

40

Example 6

[0048] The same procedure as in Example 3 was repeated except that a Compound 12 shown in Table 6 was used as the fluorine-containing phosphor derivative. The results are shown in Table 7.

45

Example 7

[0049] The same procedure as in Example 1 was repeated except that the treatment with the aqueous solution of chromium sulfate and the treatment with the aqueous solution of fluorine-containing phosphor derivative were in reverse order. The results are shown in Table 7.

50

Example 8

[0050] The same procedure as in Example 2 was repeated except that the treatment with the aqueous solution of zirconium sulfate and the treatment with the aqueous solution of fluorine-containing phosphor derivative were in reverse

55

order. The results are shown in Table 7.

Example 9

5 [0051] The same procedure as in Example 3 was repeated except that the treatment with the aqueous solution of aluminum chloride and the treatment with the aqueous solution of fluorine-containing phosphor derivative were in reverse order. The results are shown in Table 7.

Example 10

10 [0052] The same procedure as in Example 4 was repeated except that the treatment with the aqueous solution of chromium sulfate and the treatment with the aqueous solution of fluorine-containing phosphor derivative were in reverse order. The results are shown in Table 7.

15 Example 11

[0053] The same procedure as in Example 5 was repeated except that the treatment with the aqueous solution of zirconium sulfate and the treatment with the aqueous solution of fluorine-containing phosphor derivative were in reverse order. The results are shown in Table 7.

Example 12

20 [0054] The same procedure as in Example 6 was repeated except that the treatment with the aqueous solution of aluminum chloride and the treatment with the aqueous solution of fluorine-containing phosphor derivative were in reverse order. The results are shown in Table 7.

Comparative Example 1

25 [0055] The same procedure as in Example 1 was repeated except that the solution of chromium sulfate was not used. The results are shown in Table 7.

Comparative Example 2

30 [0056] Each of the same textile samples as in Example 1 was treated with TG-230 (a fluorine-containing polymeric compound, manufactured by Daikin Industries Ltd.) at a solid content of 0.125 % (a bath ratio: 40:1) at 25°C for 10 minutes. The textile sample was dried at 80°C for 3 minutes and then cured at 130°C for 3 minutes. The water repellency and the oil repellency of each textile sample were measured before and after washing the textile sample. The results are shown in Table 7.

35 Comparative Example 3

[0057] Each of the same textile samples as in Example 1 was treated with Scotch guard 233A (a fluorine-containing chromium carboxylate complex salt, manufactured by 3M Company) at a solid content of 0.125 % (a bath ratio: 40:1) at 25°C for 10 minutes. The textile sample was dried at 80°C for 3 minutes and then cured at 130°C for 3 minutes. The water repellency and the oil repellency of each textile sample were measured before and after washing the textile sample. The results are shown in Table 7.

Comparative Example 4

40 [0058] The same procedure as in Comparative Example 3 was repeated- except that the solid content was 1.5 %. The results are shown in Table 7.

[0059] In all of Comparative Examples 1 to 4, the touch, the feeling, the softness of the textile sample after the treatment were inferior to those before the treatment. These properties could not be improved by the washing.

45 Experimental Example 1

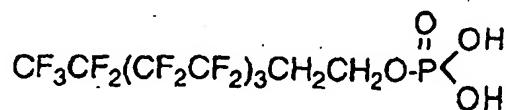
[0060] Using a colorimeter R-200 (manufactured by Minolta Camera Co., Ltd.), a color difference ΔE_{ab} between an untreated nylon-6 taffeta control and each of unwashed nylon-6 taffeta samples treated in Examples 1-6 and Compar-

ative Examples 3 and 4 was measured. The results are shown in Table 8.

5 Table 6

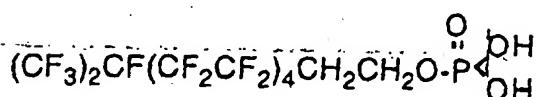
10 Compound 11:

15 Triethylamine salt of



15 Compound 12:

20 Triethylamine salt of



25

30

35

40

45

50

55

Table 7

	Nylon-6 taffeta				Habutae silk				Acrylic muslin			
	Before Wash		After Wash		Before Wash		After Wash		Before Wash		After Wash	
	Water repellency	Oil repellency										
Ex. 1	100	5	80	2	80	6	70	3	90	6	60	3
Ex. 2	90	6	60	1	90	5	60	2	70	6	60	2
Ex. 3	90	6	60	1	70	5	50	1	80	6	60	4
Ex. 4	90	5	70	2	80	5	60	3	80	6	60	3
Ex. 5	90	5	60	1	80	5	60	2	70	6	60	2
Ex. 6	90	5	60	1	70	5	60	1	80	5	60	3
Ex. 7	90	5	70	1	80	4	60	1	80	5	60	2
Ex. 8	80	5	60	1	80	4	60	1	70	5	50	1
Ex. 9	80	5	50	1	70	3	50	1	70	4	50	1
Ex. 10	80	4	60	1	80	4	50	2	70	5	50	1
Ex. 11	80	4	50	1	80	4	50	1	70	5	60	1
Ex. 12	80	4	50	1	60	3	50	1	80	5	50	1
Co. m.	50	1	0	0	50	4	0	0	50	5	50	0
Ex. 1												

Table 7 (continued)

	Nylon-6 taffeta				Habutae silk				Acrylic muslin			
	Before Wash		After Wash		Before Wash		After Wash		Before Wash		After Wash	
	Water repellency	Oil repellency										
Co. m. Ex. 2	80	1	0	0	0	0	0	0	80	2	50	0
Co. m. Ex. 3	70	0	0	0	60	0	0	0	60	0	50	0
Co. m. Ex. 4	80	2	50	0	70	2	50	0	80	2	50	0

Table 8

	Color difference ΔE_{ab}
Ex. 1	2.44
Ex. 2	0.21
Ex. 3	0.65
Ex. 4	1.88
Ex. 5	0.43
Ex. 6	0.79
Com. Ex. 3	2.90
Com. Ex. 4	10.57

5

10

Example 13First step of treatment

[0061] With immersing each of textile samples (polyester tropical for a dyeing test and nylon-6 taffeta for a dyeing test) in a 0.5 % aqueous solution of chromium sulfate (Trade name: Bay Chrom F, manufactured by Bayer AG) (a bath ratio of 10:1) at 30°C, the textile sample was stirred in a dyeing tester (manufactured by Tsuji Senki Kogyo Kabushiki Kaisha) for 30 minutes. After water was squeezed from the textile, the textile was immersed in a 0.5 % aqueous solution of a Compound 21 (a fluorine-containing phosphor derivative) shown in Table 9 (a bath ratio of 10:1) at 50°C for 30 minutes with stirring. After a 0.3 % aqueous solution of formic acid was added to a bath containing the textile sample to adjust the pH of the bath to 3, the textile sample was stirred for 30 minutes, water was squeezed from the textile sample, and the textile sample was washed with water at 40°C and dried at a room temperature.

Second step of treatment (Method A)

[0062] A fluorine-containing water- and oil-repellent [Tex guard TG - 5431 and TG-5120 (both are manufactured by Daikin Industries Ltd.), and Asahi guard LS-317 (manufactured by Asahi Glass Co., Ltd.)] was diluted with tap water to a solid content of 1 %, and isopropyl alcohol was added in an amount of 3 % to prepare a treating liquid. The sample fabric treated in the first step was immersed in the treating liquid, squeezed with a mangle to give a wet pickup of 40 % (in the case of the polyester fabric) or 25 % (in the case of the nylon fabric), dried at 110°C for 3 minutes and thermally treated at 160°C for 1 minute.

[0063] The water repellency, the oil repellency and the feeling of each textile sample were measured before and after the washing. The results are shown in Table 10. In addition, the initial hot water repellency was measured. The results are shown in Table 11.

Example 14First step of treatment

[0064] The same procedure of the first step in Example 13 was repeated.

45

Second step of treatment (Method B)

[0065] The same procedure as in the second step of Example 13 was repeated except that the treating liquid further contained Erastron BN - 69 (a blocked isocyanate manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.) in an amount of 2 % and Erastron Catalyst (a catalyst manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.) in an amount of 0.2 %.

[0066] The textile sample was evaluated as in Example 13. The results are shown in Tables 10 and 11.

Example 15

55

First step of treatment

[0067] The same procedure of the first step in Example 13 was repeated.

Second step of treatment (Method C)

5 [0068] The same procedure as in the second step of Example 13 was repeated except that the treating liquid further contained Sumitex resin M-3 (methylol melamine manufactured by Sumitomo Chemical Co., Ltd.) in an amount of 0.3 % and Sumitex accelerator (a catalyst manufactured by Sumitomo Chemical Co., Ltd.) in an amount of 0.3 %.

6 [0069] The textile sample was evaluated as in Example 13. The results are shown in Tables 10 and 11.

Comparative Example 510 Only second step (Method A)

11 [0070] Each of the same textile samples as used in Example 13 was subjected to only the second step (Method A) of Example 13. The textile sample was evaluated as in Example 13. The results are shown in Tables 10 and 11.

15 Comparative Example 6Only second step (Method B)

20 [0071] Each of the same textile samples as used in Example 13 was subjected to only the second step (Method B) of Example 14. The textile sample was evaluated as in Example 13. The results are shown in Tables 10 and 11.

Comparative Example 725 Only second step (Method C)

26 [0072] Each of the same textile samples as used in Example 13 was subjected to only the second step (Method C) of Example 15. The textile sample was evaluated as in Example 13. The results are shown in Tables 10 and 11.

Example 16

30

First step of treatment

35

[0073] The same procedure of the first step in Example 13 was repeated except that the treated textile samples were Ecsaine (a suede - type artificial leather manufactured by Toray Industries Inc.) and Soflinacial (an artificial napped leather manufactured by Kuraray Co., Ltd.).

Second step of treatment (Method A)

40

[0074] A fluorine-containing water- and oil-repellent (Tex guard TG - 5421 manufactured by Daikin Industries Ltd.) was diluted with tap water to a solid content of 1 %, and isopropyl alcohol was added in an amount of 3 % to prepare a treating liquid. The sample fabric treated in the first step was immersed in the treating liquid, squeezed with a mangle to give a wet pickup of 50 % (in both of Ecsaine and Soflinacial), dried at 110°C for 3 minutes and thermally treated at 160°C for 1 minute.

45

[0075] The water repellency, the oil repellency and the feeling of each textile sample were measured before and after the washing. The results are shown in Table 12.

Example 17

50

First step of treatment

55

[0076] The same procedure as in the first step of Example 12 was repeated except that the same textile samples as used in Example 16 were used.

60

Second step of treatment (Method B)

65

[0077] The same procedure as in the second step of Example 16 was repeated except that the treating liquid further contained Erastron BN - 69 (a blocked isocyanate manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.) in an amount of 2 % and Erastron Catalyst (a catalyst manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.) in an amount of 0.2 %.

[0078] The water repellency, the oil repellency and the feeling of each textile sample were evaluated before and after the washing. The results are shown in Table 12.

Example 18

5

First step of treatment

[0079] The same procedure as in the first step of Example 16 was repeated.

10 Second step of treatment (Method C)

[0080] The same procedure as in the second step of Example 16 was repeated except that the treating liquid further contained Sumitex resin M-3 (methylol melamine manufactured by Sumitomo Chemical Co., Ltd.) in an amount of 0.3 % and Sumitex accelerator (a catalyst manufactured by Sumitomo Chemical Co., Ltd.) in an amount of 0.3 %.

15 [0081] The water repellency, the oil repellency and the feeling of each textile sample were evaluated before and after the washing. The results are shown in Table 12.

Comparative Example 8

20 Only second step (Method A)

[0082] Each of the same textile samples as used in Example 16 was subjected to only the second treatment (Method A) of Example 16. The water repellency, the oil repellency and the feeling of the textile sample were measured before and after the washing. The results are shown in Table 12.

25

Comparative Example 9

Only second step (Method B)

30 [0083] Each of the same textile samples as used in Example 16 was subjected to only the second treatment (Method B) of Example 17. The water repellency, the oil repellency and the feeling of the textile sample were measured before and after the washing. The results are shown in Table 12.

Comparative Example 10

35

Only second step (Method C)

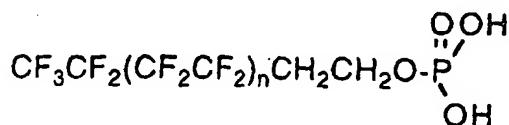
[0084] Each of the same textile samples as used in Example 16 was subjected to only the second treatment (Method C) of Example 18. The water repellency, the oil repellency and the feeling of the textile sample were measured before and after the washing. The results are shown in Table 12.

Table 9

45

Compound 21:

Triethylamine salt of



55

(a mixture of compounds wherein n is 3, 4, 5 and 6 (a molar ratio of the compounds is 5:3:2:1)

Table 10

			Water repellency			Oil repellency			Feeling		
			TG-5431	TG-5120	LS-317	TG-5431	TG-5120	LS-317	TG-5431	TG-5120	LS-317
5		Ex. 13	L ₀ L ₂₀	100+ 100+	100+ 80+	100+ 90+	7 5	5 3	7 5	O O	O O
10	Polyester Tropical	Ex. 14	L ₀ L ₂₀	100+ 90+	100+ 80+	100+ 90-	6 4	5 3	6 4	O O	O O
15		Ex. 15	L ₀ L ₂₀	100+ 100+	100+ 90	100+ 100	7 5	6 2	7 5	O O	O O
20		Com. Ex. 5	L ₀ L ₂₀	100+ 90	100+ 70	100+ 80+	6 4	5 0	6 4	Δ Δ	Δ Δ
25		Com. Ex. 6	L ₀ L ₂₀	100+ 80	100+ 80	100+ 70+	6 4	4 1	6 4	X X	Δ Δ
30		Com. Ex. 7	L ₀ L ₂₀	100+ 90+	100+ 80+	100+ 90+	6 5	6 0	6 4	X X	X X
35		Ex. 13	L ₀ L ₂₀	100+ 80+	100+ 80-	100+ 70	4 0	4 0	4 0	O O	O O
40		Ex. 14	L ₀ L ₂₀	100+ 80+	100+ 80-	100+ 80	4 0	3 0	4 0	O O	O O
45		Ex. 15	L ₀ L ₂₀	100+ 80+	100+ 80	100+ 70	5 0	4 0	4 0	O O	O O
	Note: L ₀ indicates one before the washing, and L ₂₀ indicates one after washing 20 times. The feeling is expressed as follows: O: soft, Δ: slightly hard, and X: hard.										

Table 11

		TG-5431	TG-5120	LS-317
5	Polyester tropical	Ex. 13	90+	90+
		Ex. 14	90+	90
		Ex. 15	100	90+
		Com. Ex. 5	80	70
		Com. Ex. 6	70	50
		Com. Ex. 7	80+	50
10	Nylon taffeta	Ex. 13	90+	90+
		Ex. 14	90+	90
		Ex. 15	100	90+
		Com. Ex. 5	50	50
		Com. Ex. 6	50	50
		Com. Ex. 7	50	50

Table 12

			Water repellency	Oil repellency	Feeling
25	Ecsaine	Ex. 16	L ₀	100+	6
			L ₂₀	80+	4
		Ex. 17	L ₀	100+	6
			L ₂₀	80	4
		Ex. 18	L ₀	100+	6
			L ₂₀	80+	4
		Com. Ex. 8	L ₀	100+	6
			L ₂₀	80	0
		Com. Ex. 9	L ₀	100+	6
			L ₂₀	80	2
30		Com. Ex. 10	L ₀	100+	6
			L ₂₀	80	2
35					X
					X
40					X
					X

45

50

55

Table 12 (continued)

			Water repellency	Oil repellency	Feeling		
5	Soflinacial	Ex. 16	L_0	100+	6		
			L_{20}	50	0		
		Ex. 17	L_0	100+	6		
			L_{20}	80	0		
		Ex. 18	L_0	100+	6		
			L_{20}	80	1		
		Com. Ex. 8	L_0	100+	5		
			L_{20}	0	Δ		
		Com. Ex. 9	L_0	100+	6		
			L_{20}	50	X		
10		Com. Ex. 10	L_0	100+	3		
			L_{20}	50	X		
Note: L_0 indicates one before the washing, and L_{20} indicates one after washing 20 times.							
The feeling is expressed as follows:							
○: soft,							
Δ: slightly hard, and							
X: hard.							

Example 19

30 [0085] A nylon loop pile carpet sample was stirred in a dyeing tester (manufactured by Tsujii Senki Kogyo Kabushiki Kaisha) for 30 minutes with immersed in a 0.5 % aqueous solution of chromium sulfate (trade name: Bay Chrom F, manufactured by Bay AG) (a bath ratio of 10:1) at 30°C. Water was squeezed from the sample. The sample was stirred for 30 minutes with immersed in a 0.5 % aqueous solution of Compound 21 (a fluorine-containing phosphor derivative) (a bath ratio of 10:1) shown in Table 9 at 50°C. A 0.3 % aqueous solution of formic acid was added to the bath to adjust pH of the content of the bath to 3. The carpet sample was stirred for 30 minutes and washed with water at 40°C and dried at a room temperature.

35 [0086] The dry soil releasability, the feeling before and after the rub, the water repellency and the oil repellency of the treated sample were evaluated. The results are shown in Table 13.

Example 20

40 [0087] A liquid prepared by diluting a fluorine-containing water- and oil-repellent (TG-950 manufactured by Daikin Industries Ltd. (a solid content of 30 %)) with tap water by 10 times was sprayed in an application amount of 75 g/m² on the carpet sample subjected to the treatment of Example 19 and then the carpet sample was dried at 130°C for 3 minutes. The carpet sample was evaluated in the same manner as in Example 19. The results are shown in Table 13.

Example 21

45 [0088] A liquid prepared by diluting a fluorine-containing water- and oil-repellent (TG-951 manufactured by Daikin Industries Ltd. (a solid content of 30 %)) with tap water by 10 times was sprayed in an application amount of 75 g/m² on the carpet sample subjected to the treatment of Example 19 and then the carpet sample was dried at 130°C for 3 minutes. The carpet sample was evaluated in the same manner as in Example 19. The results are shown in Table 13.

Example 22

55 [0089] A liquid prepared by diluting a fluorine-containing water- and oil-repellent (AG-800 manufactured by Asahi Glass Co., Ltd. (a solid content of 30 %)) with tap water by 10 times was sprayed in an application amount of 75 g/m² on the carpet sample subjected to the treatment of Example 19 and then the carpet sample was dried at 130°C for 3

minutes. The carpet sample was evaluated in the same manner as in Example 19. The results are shown in Table 13.

Example 23

5 [0090] A liquid prepared by diluting a silicone stainproofing agent (Bayguard AS manufactured by Bay AG (a solid content of 6 %)) with tap water by 10 times was sprayed in an application amount of 75 g/m² on the carpet sample subjected to the treatment of Example 19 and then the carpet sample was dried at 130°C for 3 minutes. The carpet sample was evaluated in the same manner as in Example 19. The results are shown in Table 13.

10 Comparative Example 11

15 [0091] A liquid prepared by diluting TG-950 with tap water by 10 times was sprayed in an application amount of 75 g/m² on the same nylon loop pile carpet sample as used in Example 19 and then the carpet sample was dried at 130°C for 3 minutes. The carpet sample was evaluated in the same manner as in Example 19. The results are shown in Table 13.

Comparative Example 12

25 [0092] A liquid prepared by diluting TG-951 with tap water by 10 times was sprayed in an application amount of 75 g/m² on the same nylon loop pile carpet sample as used in Example 19 and then the carpet sample was dried at 130°C for 3 minutes. The carpet sample was evaluated in the same manner as in Example 19. The results are shown in Table 13.

30 Comparative Example 13

35 [0093] A liquid prepared by diluting AG-800 with tap water by 10 times was sprayed in an application amount of 75 g/m² on the same nylon loop pile carpet sample as used in Example 19 and then the carpet sample was dried at 130°C for 3 minutes. The carpet sample was evaluated in the same manner as in Example 19. The results are shown in Table 13.

Comparative Example 14

40 [0094] A liquid prepared by diluting Bayguard AS with tap water by 10 times was sprayed in an application amount of 75 g/m² on the same nylon loop pile carpet sample as used in Example 19 and then the carpet sample was dried at 130°C for 3 minutes. The carpet sample was evaluated in the same manner as in Example 19. The results are shown in Table 13.

Table 13

		Feeling	Water repellency	Oil repellency	Dry soil repellency Contamination rate (%)
Ex. 19	Before rubbing	○	20	3	18
	After rubbing	○	20	3	
Ex. 20	Before rubbing	○	40	4	22
	After rubbing	○	30	4	
Ex. 21	Before rubbing	○	30	3	19
	After rubbing	○	20	3	
Ex. 22	Before rubbing	○	30	4	20
	After rubbing	○	20	4	
Ex. 23	Before rubbing	○	10	1	20
	After rubbing	○	10	0	
Com. Ex. 11	Before rubbing	△	40	4	35
	After rubbing	△	20	2	

Table 13 (continued)

		Feeling	Water repellency	Oil repellency	Dry soil releasability Contamination rate (%)
5	Com. Ex. 12	Before rubbing	Δ	30	3
		After rubbing	Δ	10	1
10	Com. Ex. 13	Before rubbing	X	30	4
		After rubbing	X	10	2
15	Com. Ex. 14	Before rubbing	Δ	0	0
		After rubbing	Δ	0	0
Note: Dry soil releasability: The contamination rate of the untreated textile was 54 %.					

Reference Example 1 (Example showing the preparation of a test fabric)

[0095] A wool muslin fabric for a dyeing test was stirred in a dyeing tester (manufactured by Tsuji Senki Kogyo Kabushiki Kaisha) for 10 minutes with immersed in an aqueous hydrochloric acid solution having a temperature of 25°C (the amounts of water and 35 % concentrated hydrochloric acid were 3,000 % and 6 %, respectively, based on the fabric sample). An aqueous solution of sodium hypochlorite was added so that the amount of active chlorine concentration was 1 % by weight based on the fabric sample and then the sample was further stirred for 30 minutes. The content of the bath was removed and an aqueous solution of sodium carbonate having a temperature of 25°C (the amounts of water and sodium carbonate were 3,000 % and 4 %, respectively, based on the fabric sample) was charged in the bath so that the fabric was immersed therein. Sodium sulfite in an amount of 4 % based on the fabric sample was added to the bath and the sample was stirred for 10 minutes. The content of the bath was removed, the sample was washed with water and air-dried to give a descaled wool fabric sample.

Example 24

[0096] Each of two textile samples (a descaled wool fabric sample prepared in Reference Example 1; and a nylon-6 fabric for a dyeing test) was stirred in a dyeing tester (manufactured by Tsuji Senki Kogyo Kabushiki Kaisha) for 30 minutes with immersed in a 0.5 % aqueous solution of chromium sulfate (trade name: Bay Chrom F manufactured by Bay AG) (a bath ratio of 10:1) at 30°C. Water was-squeezed from the sample. The sample was stirred for 30 minutes with immersed in a 0.5 % aqueous solution of Compound 31 (a fluorine-containing phosphor derivative) (a bath ratio of 10:1) shown in Table 14 at 50°C. A 0.3 % aqueous solution of formic acid was added to the bath to adjust pH of the content in the bath to 3. The fabric sample was stirred for 30 minutes and water was squeezed from the fabric sample. The fabric sample was washed with water at 40°C and dried at a room temperature.

[0097] The water repellency, the oil repellency and the feeling of the treated textile sample were measured before and after the washing. The results are shown in Table 15.

Example 25First step of treatment

[0098] The same procedure as in Example 24 was repeated.

Second step of treatment (Method A)

[0099] A fluorine-containing water- and oil-repellent (Tex guard TG - 5431 manufactured by Daikin Industries Ltd.) was diluted with tap water to a solid content of 1 %, and isopropyl alcohol was added in an amount of 3 % to prepare a treating liquid. The fabric sample treated in the first step was immersed in the treating liquid, squeezed with a mangle to give a wet pickup of 65 % (for the wool fabric) or 25 % (for the nylon fabric), dried at 110°C for 3 minutes and thermally treated at 160°C for 1 minute.

[0100] The fabric was evaluated in the same manner as in Example 24. The results are shown in Table 15.

Example 26First step of treatment

5 [0101] The same procedure as in Example 24 was repeated.

Second step of treatment (Method B)

10 [0102] The same procedure as in the second step of Example 25 was repeated except that the treating liquid further contained Erastron BN - 69 (a blocked isocyanate manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.) in an amount of 2 % and Erastron Catalyst (a catalyst manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.) in an amount of 0.2 %.

15 [0103] The fabric was evaluated in the same manner as in Example 24. The results are shown in Table 15.

Example 27

15

First step of treatment

20 [0104] The same procedure as in Example 24 was repeated.

Second step of treatment (Method C)

25 [0105] The same procedure as in the second step of Example 25 was repeated except that the treating liquid further contained Sumitex resin M-3 (methylol melamine manufactured by Sumitomo Chemical Co., Ltd.) in an amount of 0.3 % and Sumitex Accelerator (a catalyst manufactured by Sumitomo Chemical Co., Ltd.) in an amount of 0.3 %.

25 [0106] The fabric was evaluated in the same manner as in Example 24. The results are shown in Table 15.

Example 28

30 [0107] The same procedure as in Example 24 was repeated except that Compound 32 shown in Table 14 was used as the fluorine - containing phosphor derivative. The results are shown in Table 15.

Example 29

35 [0108] The same procedure as in Example 25 was repeated except that Compound 32 was used as the fluorine-containing phosphor derivative. The results are shown in Table 15.

Example 30

40 [0109] The same procedure as in Example 26 was repeated except that Compound 32 was used as the fluorine-containing phosphor derivative. The results are shown in Table 15.

Example 31

45 [0110] The same procedure as in Example 27 was repeated except that Compound 32 was used as the fluorine-containing phosphor derivative. The results are shown in Table 15.

Comparative Example 15Only second step (Method A)

50 [0111] Each of the same textile samples as used in Example 24 was subjected to only the second step (Method A) of Example 25. The samples were evaluated as in Example 24. The results are shown in Table 15.

Comparative Example 16Only second step (Method B)

55 [0112] Each of the same textile samples as used in Example 24 was subjected to only the second step (Method B)

of Example 26. The samples were evaluated as in Example 24. The results are shown in Table 15.

Comparative Example 17

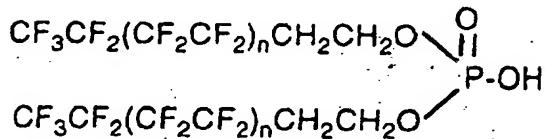
5 Only second step (Method C)

[0113] Each of the same textile samples as used in Example 24 was subjected to only the second step (Method C) of Example 27. The samples were evaluated as in Example 24. The results are shown in Table 15.

Table 14

Compound 31:

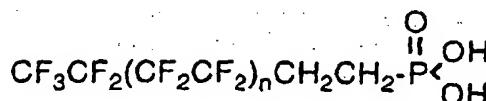
Diethanolamine salt of



25 (a mixture of compounds wherein n is 3, 4, 5 and 6 (a molar ratio of the compounds is 5:3:2:1))

Compound 32:

[0114] Triethylamine salt of



(a mixture of compounds wherein n is 3, 4, 5 and 6 (a major ratio of the compounds is 5:3:2:1))

Table 15

		Descaled wool			Nylon taffeta		
		Feeling	Water repellency	Oil repellency	Feeling	Water repellency	Oil repellency
Ex. 24	L ₀	○	100+	6	○	100	6
	L ₂₀	○	90+	2	○	70	4
Ex. 25	L ₀	○	100+	6	○	100	6
	L ₂₀	○	90	2	○	100	6
Ex. 26	L ₀	○	100+	6	○	100	6
	L ₂₀	○	90+	3	○	80+	5
Ex. 27	L ₀	○	100+	6	○	100	6
	L ₂₀	○	100	3	○	80+	5

Table 15 (continued)

		Descaled wool			Nylon taffeta			
		Feeling	Water repellency	Oil repellency	Feeling	Water repellency	Oil repellency	
5	Ex. 28	L ₀	○	100+	6	○	100+	4
		L ₂₀	○	70	0	○	80	0
10	Ex. 29	L ₀	○	100+	6	○	100+	4
		L ₂₀	○	70	0	○	80	0
15	Ex. 30	L ₀	○	100+	6	○	100+	4
		L ₂₀	○	80+	0	○	80	0
20	Ex. 31	L ₀	○	100+	6	○	100+	4
		L ₂₀	○	80	0	○	80	0
25	Com. Ex. 15	L ₀	△	100+	6	△	100+	4
		L ₂₀	△	50	0	△	70	0
30	Com. Ex. 16	L ₀	X	100+	6	X	100+	4
		L ₂₀	X	50	0	X	70	0
35	Com. Ex. 17	L ₀	X	100+	6	X	100+	4
		L ₂₀	X	50	0	X	0	0

Note: L₀ indicates one before the washing, and L₂₀ indicates one after washing 20 times.

The feeling is expressed as follows:

○: soft,
 △: slightly hard, and
 X: hard.

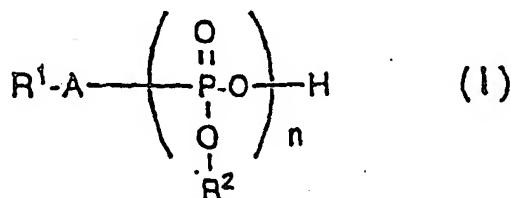
Effect of the Invention

35 [0115] According to the present invention, the touch, feeling, color shade and softness originally possessed by the fibers can be kept after the textile is treated. The present invention can keep the above properties at desired levels even if the textile is subjected to a long time use in which the textile is washed or rubbed. The present invention can impart to the textile the hot water repellency, the durable water- and oil-repellency and the resistance to contamination.

Claims

1. Use of an agent for treating textile comprising a combination of a modifying agent and a fixing agent, wherein the modifying agent is a fluorine-containing phosphor derivative represented by the formula:

45



50

wherein R¹ and R² are, same or different, a hydrogen atom or R_f(CH₂)_m, wherein R_f is a saturated or unsaturated, linear or branched fluorine-containing aliphatic group having 4 to 20 carbon atoms, and an oxygen atom, a nitrogen atom, a sulfonyl group and/or an aromatic ring may be inserted between the carbon atoms, and m is 1 or 2, and

5 wherein R¹ and R² are not simultaneously a hydrogen atom,
 A is an oxygen atom, a sulfur atom or a direct bond, and
 n is 1 or 2,
 and having a molecular weight of not larger than 2000 or a salt thereof, and the fixing agent is a metal salt compound.

10 2. Use of the agent for treating textile according to claim 1, wherein the metal salt compound is at least one selected from the group consisting of chlorides, nitrate salts, sulfate salts and hydroxides of a metal having a valency of at least

15 3. Use of the agent for treating textile according to claim 2, wherein the metal having the valency of at least two is at least one selected from the group consisting of Cr, Zr, Ti and Al.

20 4. A method for treating a textile wherein the modifying agent and the fixing agent as defined in claim 1 are used for the treatment.

25 5. The method according to claim 4, wherein the textile is treated with the fixing agent and then with the modifying agent.

30 6. The method according to claim 4, wherein the textile is treated with the modifying agent and then with the fixing agent.

35 7. The method according to claim 4, wherein the textile is treated with the fixing agent and the modifying agent simultaneously.

40 8. The method according to claim 4, **characterized in**, that the textile is subsequently treated with a fluorine-containing water- and oil-repellent.

45 9. The method according to Claim 5 to 7, **characterized in** that the textile is subsequently treated with a fluorine-containing water- and oil-repellent.

50 10. A method according to any of claims 4 to 9, **characterized in**, that the textile is a carpet.

55 11. The method according to Claim 10, **characterized in**, that the carpet is subsequently treated with a fluorine-containing stainproofing agent.

60 12. A textile which is treated with the method according to anyone of claims 4 to 9 and which comprises a modifying agent and a fixing agent as defined in claim 1.

65 13. The textile according to claim 12, which is at least one selected from the group consisting of a fiber as such, a yarn, and a woven, knitted and nonwoven fabric.

70 14. The textile according to claim 12, wherein the textile comprises a natural fiber and/or a synthetic fiber.

75 15. The textile according to claim 14, wherein the natural fiber is at least one selected from the group consisting of cotton, wool and silk.

80 16. The textile according to claim 14, wherein the natural fiber is at least one selected from the group consisting of cotton, wool and silk.

85 17. The textile according to claim 14, which comprises a protein fiber and/or a polyamide fiber.

90 18. The textile according to claim 12, which is at least one selected from the group consisting of an extra fine fiber as such, and a yarn, a woven fabric, a knitted fabric and a nonwoven fabric formed from the extra fine fiber.

95 19. The textile according to claim 12, which is an artificial leather comprising the extra fine fiber.

100 20. The textile according to Claim 18 or 19, wherein the diameter of the extra fine fiber is not larger than 0.11 tex (1 denier).

21. The textile according to Claim 18 or 19, wherein the diameter of the extra fine fiber is from 0.11 tex to 0.000011 tex (1.0 to 0.0001 denier).

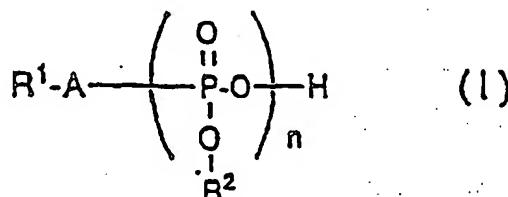
5 22. A carpet comprising a yarn treated with the method according to anyone of claims 4 to 9 and which comprises a modifying agent and a fixing agent as defined in claim 1.

10 23. A carpet which is treated by the method according to claim 10 and which comprises a modifying agent and a fixing agent as defined in claim 1.

15 24. Use of a textile according to Claim 12 for a tent, an automobile cover, a cover for two-wheeled vehicle, a convertible top for a load-carrying platform of a truck, a covering sheet for construction work, an umbrella, clothes, rainwear clothes, a hat, a cap, a foot wear, a suitcase, a bag, a cover of an article for sitting down, a curtain, a rug or mat, an interior article for a wall or ceiling of a built structure or vehicle.

15 **Patentansprüche**

20 1. Verwendung eines Mittels zur Behandlung eines Textils umfassend eine Kombination aus einem Modifikationsmittel und einem Fixierungsmittel, wobei das Modifikationsmittel ein Fluor enthaltendes Phosphorderivat ist, dar-
25 gestellt durch die Formel:



35 worin R^1 und R^2 gleich oder verschieden sind und ein Wasserstoffatom oder $R_f-(CH_2)_m-$, worin R_f eine gesättigte oder ungesättigte lineare oder verzweigte Fluor enthaltende aliphatische Gruppe mit 4 bis 20 Kohlenstoffatomen ist und ein Sauerstoffatom, ein Stickstoffatom, eine Sulfonylgruppe und/oder aromatischer Ring zwischen den Kohlenstoffatomen eingeführt sein kann, darstellen und m 1 oder 2 ist, und worin R^1 und R^2 nicht gleichzeitig ein Wasserstoffatom sind, darstellen,

40 A ein Sauerstoffatom, ein Schwefelatom oder eine direkte Bindung ist und
n 1 oder 2 ist,

45 und mit einem Molekulargewicht von nicht größer als 2000 oder ein Salz davon, und das Fixierungsmittel eine Metallsalzverbindung ist.

2. Verwendung des Mittels zur Behandlung eines Textils nach Anspruch 1, wobei die Metallsalzverbindung mindestens eine ausgewählt aus der Gruppe, bestehend aus Chloriden, Nitratsalzen, Sulfatsalzen und Hydroxiden eines Metalls mit einer Wertigkeit von mindestens 2 ist.

45 3. Verwendung des Mittels zur Behandlung von Textilien nach Anspruch 2, wobei das Metall mit der Wertigkeit von mindestens 2 mindestens eines ist ausgewählt aus der Gruppe, bestehend aus Cr, Zr, Ti und Al ist.

50 4. Verfahren zur Behandlung eines Textils, wobei das Modifizierungsmittel und das Fixierungsmittel so wie in Anspruch 1 definiert sind zur Behandlung verwendet werden.

5. Verfahren gemäß Anspruch 4, wobei das Textil mit dem Fixierungsmittel und anschließend mit dem Modifikationsmittel behandelt wird.

55 6. Verfahren gemäß Anspruch 4, worin das Textil mit dem Modifikationsmittel und anschließend mit dem Fixierungsmittel behandelt wird.

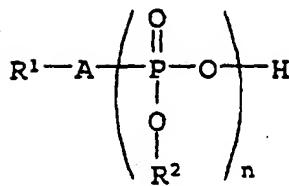
7. Verfahren gemäß Anspruch 4, wobei das Textil mit dem Fixierungsmittel und dem Modifikationsmittel gleichzeitig

behandelt wird.

8. Verfahren gemäß Anspruch 4, dadurch gekennzeichnet, dass das Textil anschließend mit einem Fluor enthaltenden Wasser- und/oder Ölabstoßer behandelt wird.
9. Verfahren nach Anspruch 5 bis 7, dadurch gekennzeichnet, dass das Textil mit einem Fluor enthaltenden Was- und/oder Ölabstoßer behandelt wird.
10. Verfahren nach Anspruch 4 bis 9, dadurch gekennzeichnet, dass das Textil ein Teppich ist.
11. Verfahren nach Anspruch 10, dadurch gekennzeichnet, dass der Teppich anschließend mit einem Fluor enthaltenden Fleckenimprägniermittel behandelt wird.
12. Textil, das mit dem Verfahren nach einem der Ansprüche 4 bis 9 behandelt wird und das ein Modifikationsmittel und Fixierungsmittel wie in Anspruch 1 umfasst.
13. Textil nach Anspruch 12, das mindestens ausgewählt ist aus der Gruppe, bestehend aus einer Faser, wie einem Garn, einem Gewebe, einem Gewirke und einem Vlies.
14. Textil nach Anspruch 12, wobei das Textil eine natürliche Faser und/oder eine synthetische Faser umfasst.
15. Textil nach Anspruch 14, wobei die natürliche Faser mindestens eine ausgewählt aus der Gruppe, bestehend aus Baumwolle, Wolle und Seide ist.
16. Textil nach Anspruch 14, wobei die natürliche Faser mindestens eine ausgewählt aus der Gruppe, bestehend aus Baumwolle, Wolle und Seide ist.
17. Textil nach Anspruch 14, das eine Proteinfaser und/oder Polyamidfaser umfasst.
18. Textil nach Anspruch 12, das mindestens eines ausgewählt aus der Gruppe, bestehend aus einer extrafeinen Faser, wie einem Garn, einem Stoff, einem Gewirke und einem Vlies, die aus der extrafeinen Faser gebildet sind, ist.
19. Textil nach Anspruch 12, das ein künstliches Leder umfassend die extrafeine Faser ist.
20. Textil nach Anspruch 18 oder 19, wobei der Durchmesser der extrafeinen Faser nicht größer als 0,11 tex (1 Denier) ist.
21. Textil nach Anspruch 18 oder 19, wobei der Durchmesser der extrafeinen Faser von 0,11 tex bis 0,000011 tex (1,0 bis 0,0001 Denier) ist.
22. Teppich, umfassend ein Garn, das mit dem Verfahren nach einem der Ansprüche 4 bis 9 behandelt ist und das ein Modifikationsmittel und ein Fixierungsmittel, wie in Anspruch 1 definiert, umfasst.
23. Teppich, der mit dem Verfahren nach Anspruch 10 behandelt ist und der ein Modifikationsmittel und ein Fixierungsmittel wie in Anspruch 1 definiert umfasst.
24. Verwendung eines Textils nach Anspruch 12 für ein Zelt, eine Autoabdeckung, eine Abdeckung für ein Zweirad, ein konvertierbares Dach einer Last tragenden Plattform eines Lastwagens, eine Abdeckdecke bei Bauarbeiten, einen Regenschirm, Kleidung, Regenkleidung, einen Hut, eine Kappe, Fußbekleidung, einen Koffer, eine Tasche, eine Abdeckung für einen Gegenstand, um darauf zu sitzen, einen Vorhang, einen Vorleger oder eine Matte, einen Innenartikel für eine Wand oder eine Decke einer Baustuktur oder eines Beförderungsmittels.

55 Revendications

1. Utilisation d'un agent de traitement de textile comprenant une combinaison d'un agent modificateur et d'un agent fixateur, dans laquelle l'agent modificateur est un dérivé de phosphore contenant du fluor représenté par la formule :



(I)

15 dans laquelle R¹ et R², identiques ou différents, sont un atome d'hydrogène ou R_f(CH₂)_m, où R_f est un groupe aliphatique saturé ou insaturé, linéaire ou ramifié et contenant du fluor ayant de 4 à 20 atomes de carbone, et un atome d'oxygène, un atome d'azote, un groupe sulfonyle et/ou un noyau aromatique peut être inséré entre les atomes de carbone, et m vaut 1 ou 2, et dans laquelle R¹ et R² ne sont pas simultanément un atome d'hydrogène,

20 A est un atome d'oxygène, un atome de soufre ou une liaison directe, et

n vaut 1 ou 2,

et ayant une masse moléculaire non supérieure à 2000, ou un sel de celui-ci, et l'agent fixateur est un composé de sel métallique.

25 2. Utilisation d'un agent de traitement de textile selon la revendication 1, dans lequel le composé de sel métallique est au moins un composé choisi dans le groupe comprenant des sels chlorures, des sels nitrates, des sels sulfates et des hydroxydes d'un métal ayant une valence d'au moins deux.

30 3. Utilisation d'un agent de traitement de textile selon la revendication 2, dans lequel le métal ayant une valence d'au moins deux est au moins un métal choisi dans le groupe comprenant Cr, Zr, Ti et Al.

4. Procédé de traitement d'un textile, dans lequel l'agent modificateur et l'agent fixateur tels que définis dans la revendication 1 sont utilisés pour le traitement.

35 5. Procédé selon la revendication 4, dans lequel le textile est traité avec l'agent fixateur et ensuite avec l'agent modificateur.

6. Procédé selon la revendication 4, dans lequel le textile est traité avec l'agent modificateur et ensuite avec l'agent fixateur.

7. Procédé selon la revendication 4, dans lequel le textile est traité simultanément avec l'agent fixateur et l'agent modificateur.

40 8. Procédé selon la revendication 4, caractérisé en ce que le textile est ensuite traité avec un agent repoussant l'eau et les huiles contenant du fluor.

9. Procédé selon les revendications 5 à 7, caractérisé en ce que le textile est ensuite traité avec un agent repoussant l'eau et les huiles contenant du fluor.

45 10. Procédé selon l'une quelconque des revendications 4 à 9, caractérisé en ce que le textile est un tapis.

11. Procédé selon la revendication 10, caractérisé en ce que le tapis est ensuite traité avec un agent antitaches contenant du fluor.

50 12. Textile traité par le procédé selon l'une quelconque des revendications 4 à 9 et comprenant un agent modificateur et un agent fixateur tels que définis dans la revendication 1.

13. Textile selon la revendication 12, qui est au moins un textile choisi dans le groupe comprenant une fibre en tant que telle, un filé et une toile tissée, tricotée et non tissée.

55 14. Textile selon la revendication 12, dans lequel le textile comprend une fibre naturelle et/ou une fibre synthétique.

15. Textile selon la revendication 14, dans lequel la fibre naturelle est au moins une fibre choisie dans le groupe comprenant le coton, la laine et la soie.
- 5 16. Textile selon la revendication 14, dans lequel la fibre naturelle est au moins une fibre choisie dans le groupe comprenant le coton, la laine et la soie.
- 10 17. Textile selon la revendication 14, comprenant une fibre protéinique et/ou une fibre de polyamide.
18. Textile selon la revendication 12, qui est au moins un textile choisi dans le groupe comprenant une fibre extra fine en tant que telle et un filé, une toile tissée, une toile tricotée et une toile non tissée formée à partir de la fibre extra fine.
19. Textile selon la revendication 12, qui est un cuir artificiel comprenant la fibre extra fine.
- 15 20. Textile selon la revendication 18 ou la revendication 19, dans lequel le diamètre de la fibre extra fine n'est pas plus grand que 0,11 tex (1 denier).
21. Textile selon la revendication 18 ou la revendication 19, dans lequel le diamètre de la fibre extra fine est de 0,11 tex à 0,000011 tex (1,0 à 0,0001 denier).
- 20 22. Tapis comprenant un filé traité par le procédé selon l'une quelconque des revendications 4 à 9 et qui comprend un agent modificateur et un agent fixateur tels que définis dans la revendication 1.
- 25 23. Tapis qui est traité par le procédé selon la revendication 10 et qui comprend un agent modificateur et un agent fixateur tels que définis dans la revendication 1.
24. Utilisation d'un textile selon la revendication 12 pour une tente, une housse pour automobile, une housse pour véhicule à deux roues, une bâche convertible pour un plateau porteur de camion, un film de couverture pour un chantier de construction, un parapluie, des vêtements, des vêtements de pluie, un chapeau, une casquette, une chaussure, une valise, un sac, une housse pour un article destiné à s'asseoir, un rideau, un tapis ou un paillasson, un article d'intérieur pour un mur ou un plafond d'une structure bâtie ou d'un véhicule.

35

40

45

50

55